

[54] SEPARATION OF PICOLINE ISOMERS

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[52] U.S. Cl. 546/353; 210/690

[58] Field of Search 546/353; 210/690

[56] References Cited

U.S. PATENT DOCUMENTS

B 426,274	1/1976	Hedge	260/674 SA
2,516,370	7/1950	Cracas	260/290
2,728,771	12/1955	Williams et al.	260/290
2,767,187	10/1956	Shrader et al.	260/270
2,924,602	2/1960	von Dohlen et al.	260/290
3,029,242	4/1962	Fleck et al.	546/353
3,064,002	11/1962	Fleck et al.	260/290
3,095,420	6/1963	Schaeffer	260/290
3,112,322	11/1963	Fotis et al.	260/283
3,626,020	3/1969	Neuzil	260/674 SA
3,663,638	5/1972	Neuzil	260/674 SA
3,665,046	5/1972	De Rosset	260/674 SA
3,668,266	6/1972	Chen et al.	260/674
3,686,343	8/1972	Bearden, Jr. et al.	260/674 SA
3,700,744	10/1972	Berger et al.	260/668 A
3,734,974	5/1973	Neuzil	260/674 SA
3,894,109	7/1975	Rosback	260/674 SA
3,997,620	12/1976	Neuzil	260/674 SA

FOREIGN PATENT DOCUMENTS

110867 12/1975 German Democratic Rep.
564363 7/1975 Switzerland

OTHER PUBLICATIONS

Wolf, F. et al, "On the Absorption of Light Pyridine Bases on Zeolitic Molecular Sieves", Z. Chem., vol. 16(4), 1976, pp. 156-157.

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[57] ABSTRACT

A process for separating alpha or gamma-picoline from a feed mixture comprising alpha-picoline or gamma-picoline and at least one other picoline isomer from which the alpha or gamma isomer is to be separated. The feed mixture is contacted at adsorption conditions with an adsorbent comprising a type Y zeolite having alkaline earth or iron group cations at exchangeable cationic sites, which exclude the alpha isomer, or with a potassium exchanged type X zeolite or calcium exchanged type Y zeolite which are selective for the gamma isomer. The high purity alpha or gamma isomer is recovered as a raffinate or extract product, respectively. Pyridine is a preferred desorbent material.

19 Claims, 5 Drawing Figures

Figure 1

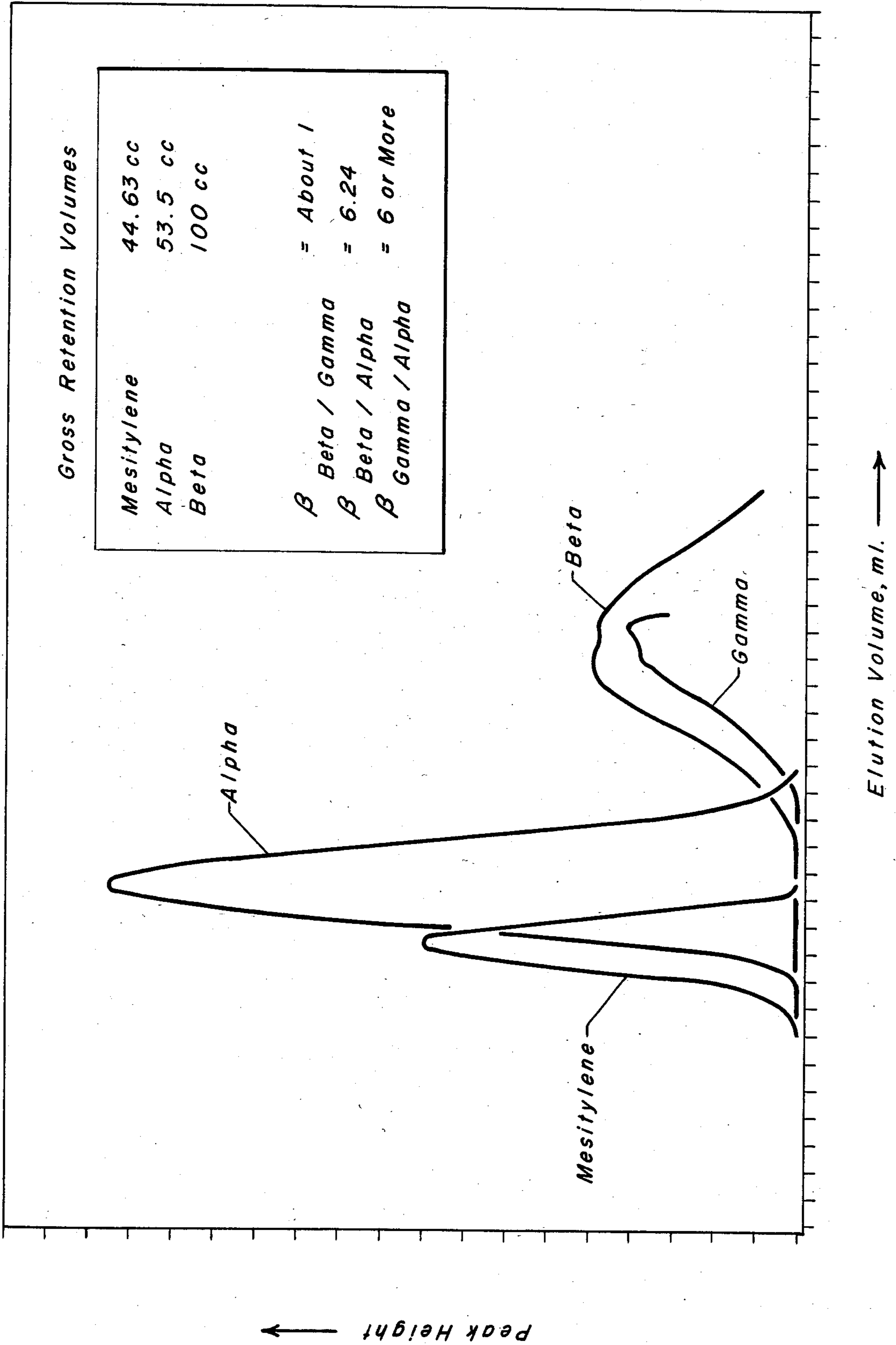


Figure 2

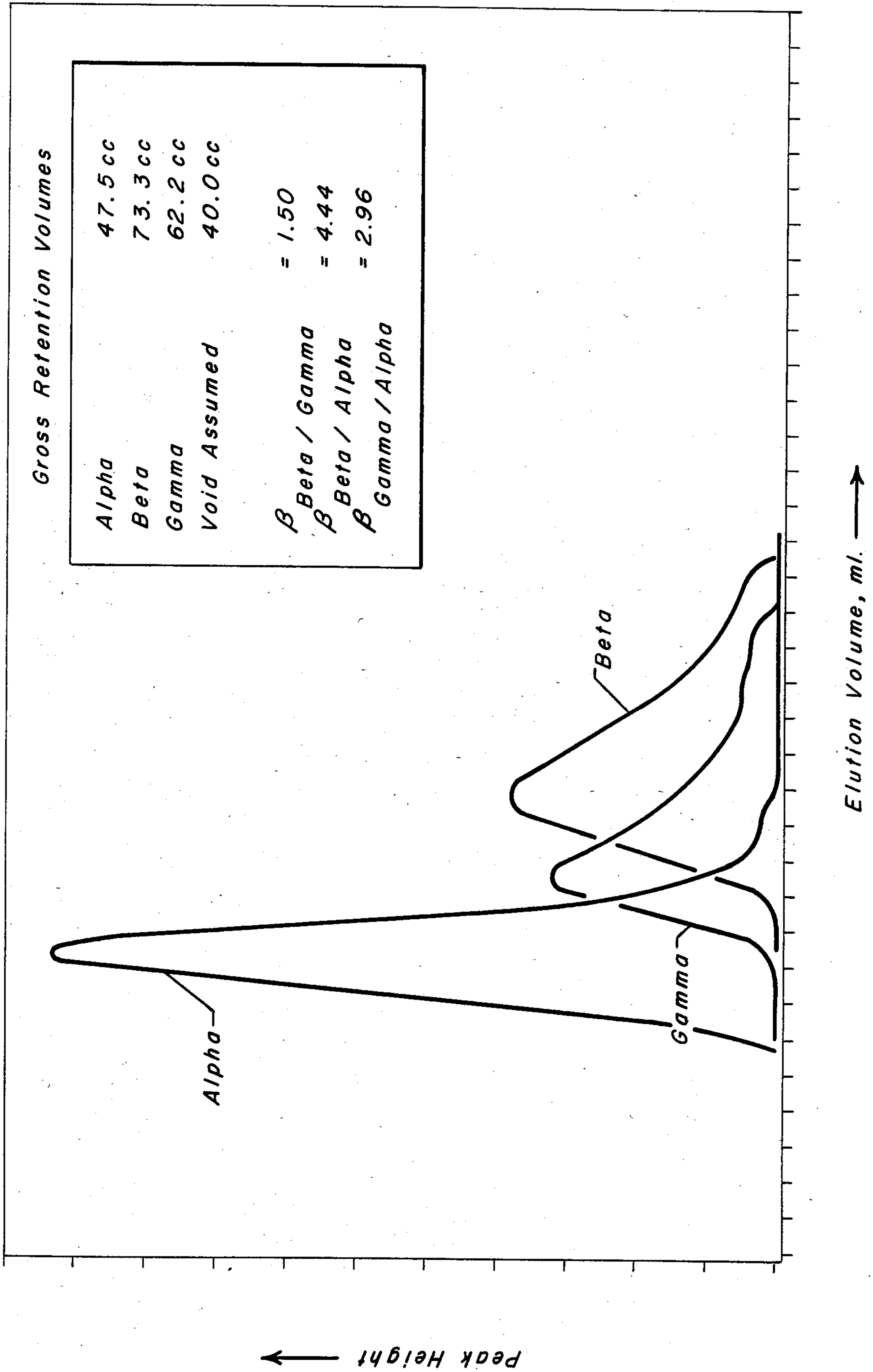


Figure 3

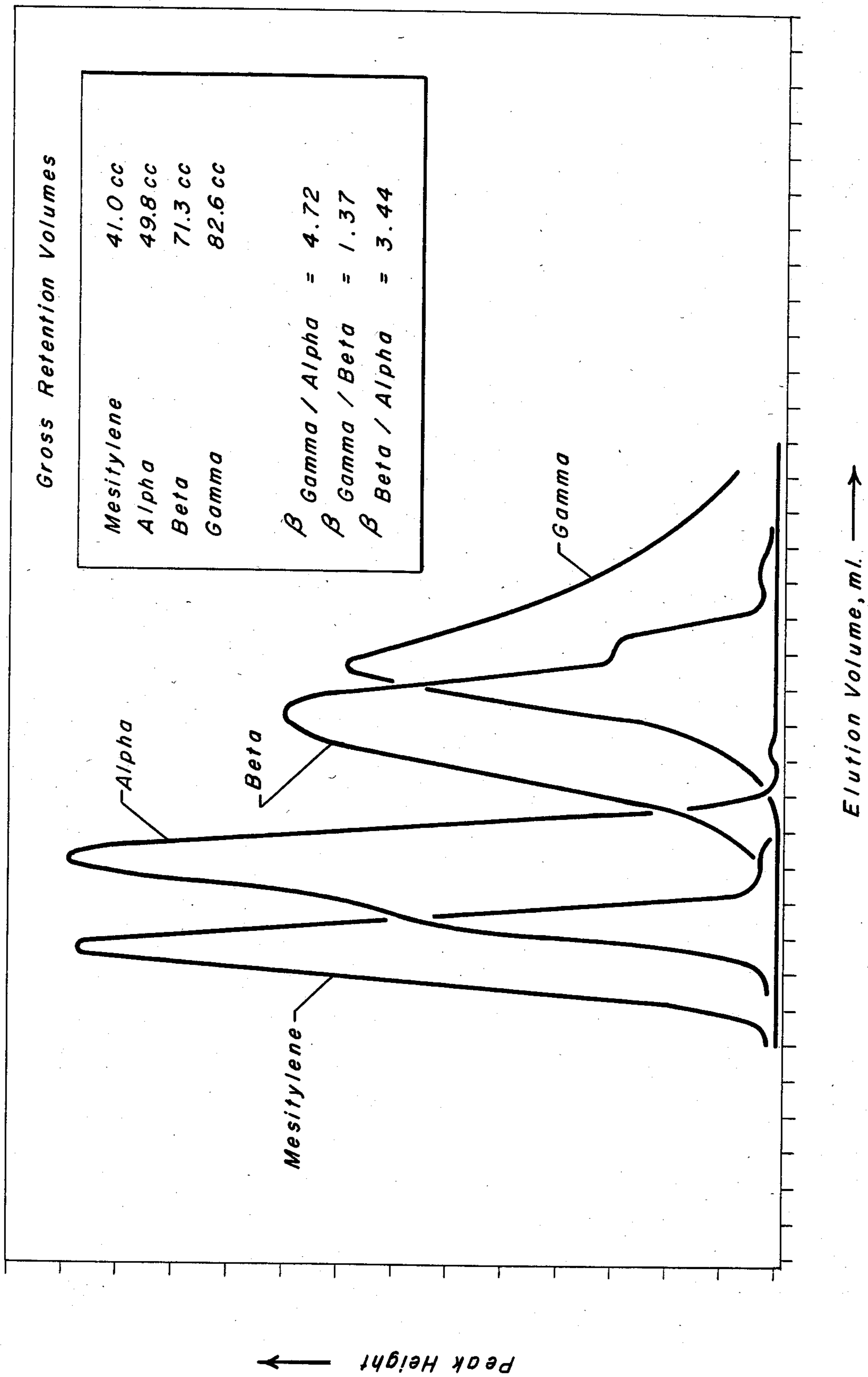


Figure 4

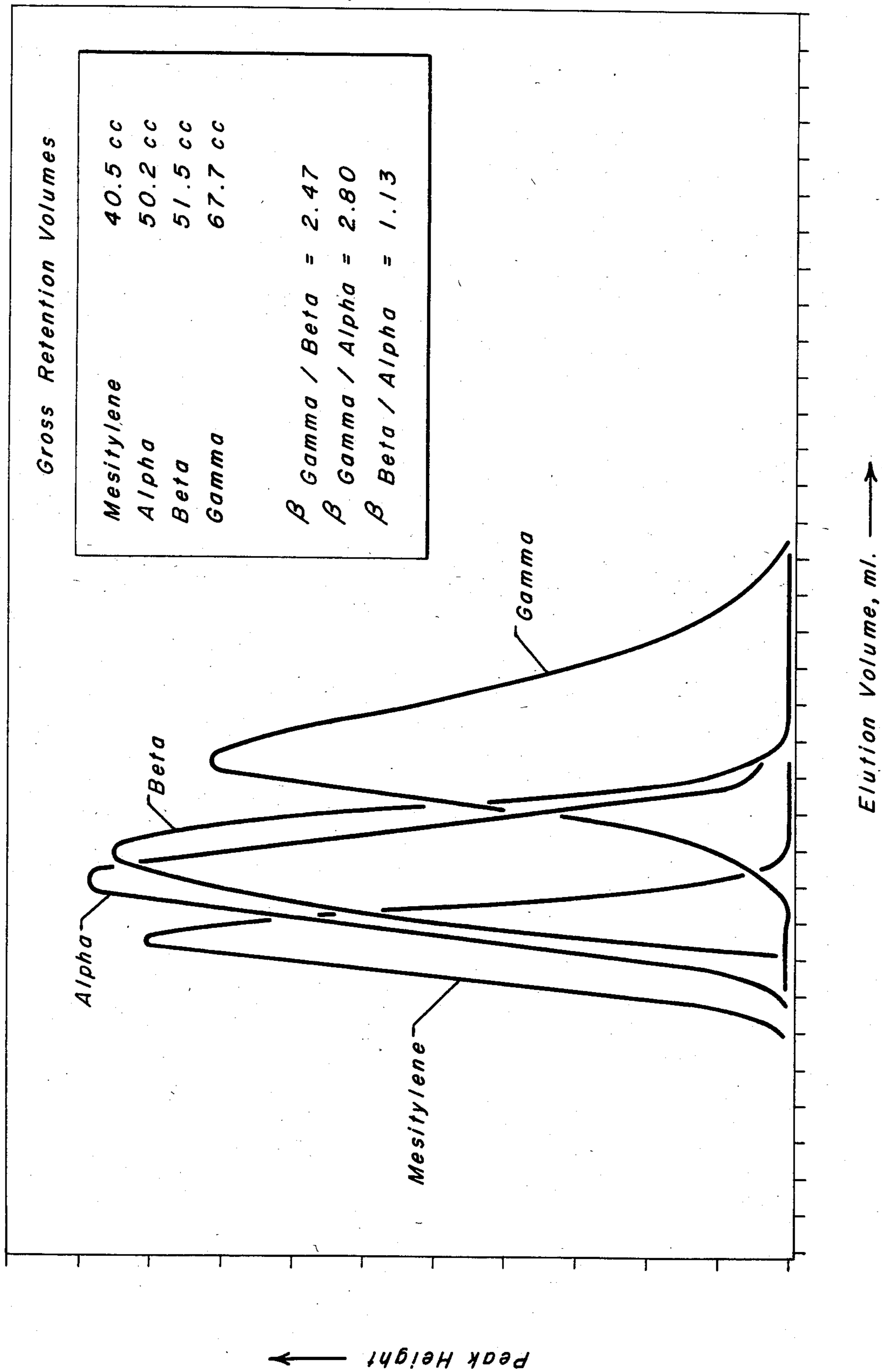
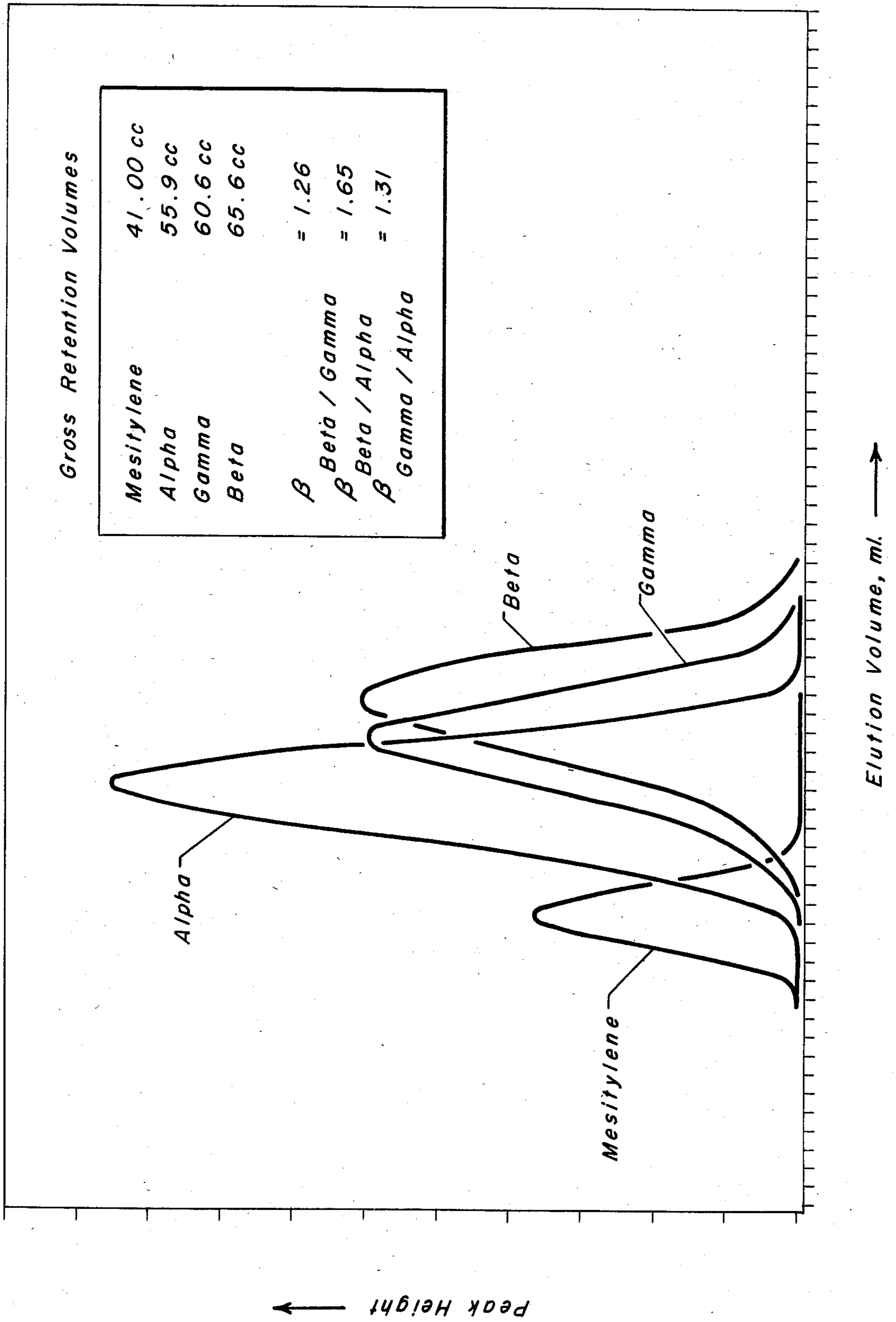


Figure 5



SEPARATION OF PICOLINE ISOMERS

BACKGROUND OF THE INVENTION

The field of art to which the claimed invention pertains is the separation of chemical isomers, and more specifically, separation of the isomers of picoline through the employment of a bed of adsorbent.

BACKGROUND INFORMATION

There is a wealth of teachings of various methods to effect the separation of isomers of picoline. These teachings, for the most part, involve conversion of one or more of the picoline isomers to corresponding intermediate chemical species which are more readily separable by physical means, followed by the conversion of each converted species to its corresponding picoline isomer. Specific examples of such separations are as taught in U.S. Pat. Nos. 2,516,370 to Cracas (mixed picoline phthalates as the intermediates); 2,728,771 to Williams et al. (oxalate salt of gamma picoline as the intermediate); 2,767,187 to Shrader et al. (betapicoline copper complex as the intermediate); 3,095,420 to Schaeffer (Werner complexes as intermediates); and 3,112,322 to Fotis, et al., (B-picoline-alkali halide complex as an intermediate).

Other references teach separation of picoline isomers directly by physical means, such as selective precipitation with a borate ester from which the desired isomers may be distilled (U.S. Pat. No. 2,924,602 to von Dohlen et al.), or by extractive distillation with ethylene glycol (Swiss Patent No. 564,363).

It is also well known that adsorbents comprising type X or Y zeolites are effective in processes to separate individual hydrocarbon isomers. In the processes described, for example, in U.S. Pat. Nos. 3,626,020 to Neuzil; 3,663,638 to Neuzil; 3,665,046 to de Rosset; 3,668,266 to Chen et al.; 3,686,343 to Bearden Jr. et al.; 3,700,744 to Berger et al.; 3,734,974 to Neuzil; 3,894,109 to Rosback; 3,997,620 to Neuzil and B426,274 to Hedge, particular zeolitic adsorbents are used to separate the para isomer of bi-alkyl substituted monocyclic aromatics from the other isomers, particularly para-xylene from other xylene isomers.

Finally, there are processes known for separating pyridine homologues employing adsorbents such as X or Y type zeolites. U.S. Pat. No. 3,064,002 to Fleck et al. and East German Patent No. 110,867 to Wolf et al. teach the adsorptive separation with X or Y-type zeolites of the homologues lutidine (dimethylpyridine) and picoline (methylpyridine). These references, however, give no hint to the separation of the individual picoline isomers.

The present invention is based on the surprising discovery that certain zeolites will in fact effect a separation of isomers of picoline from each other.

SUMMARY OF THE INVENTION

In brief summary the present invention is, in one embodiment, a process for separating alpha-picoline from a feed mixture comprising alpha-picoline and at least one other isomer of picoline. The process comprises contacting the mixture at adsorption conditions with an adsorbent comprising a type Y zeolite having alkaline earth or iron group cations at exchangeable cationic sites. The other isomer is selectively adsorbed to the substantial exclusion of the alpha isomer, and

high purity alpha-picoline is recovered as a raffinate stream.

In a second embodiment, the present invention is a process for separating gamma-picoline from a feed mixture comprising gamma-picoline and at least one other isomer of picoline. The process comprises contacting the mixture at adsorption conditions with an adsorbent comprising a type X zeolite having potassium cations at exchangeable cationic sites, or a type Y zeolite having calcium cations at exchangeable cationic sites, selectively adsorbing the gamma isomer to the substantial exclusion of the remaining isomers, removing the remaining isomers from contact with the adsorbent, and thereafter recovering high purity gamma-picoline.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-5 comprise chromatographic traces showing elution of picoline isomers.

DESCRIPTION OF THE INVENTION

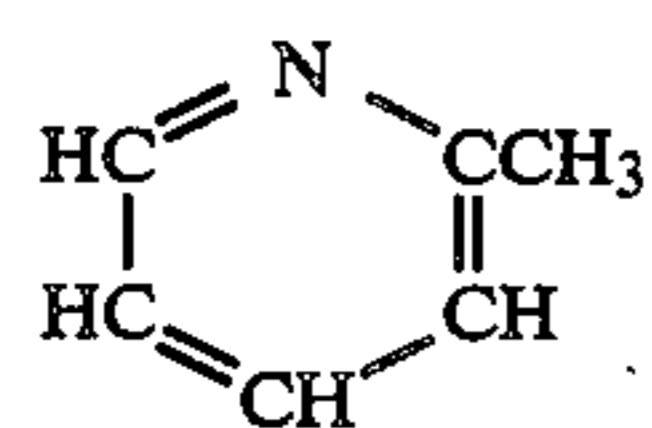
At the outset the definitions of various terms used throughout this specification will be useful in making clear the operation, objects and advantages of the present invention.

A "feed mixture" is a mixture containing one or more extract components and one or more raffinate components to be fed to an adsorbent of the process. The term "feed stream" indicates a stream of feed mixture which passes to an adsorbent used in the process.

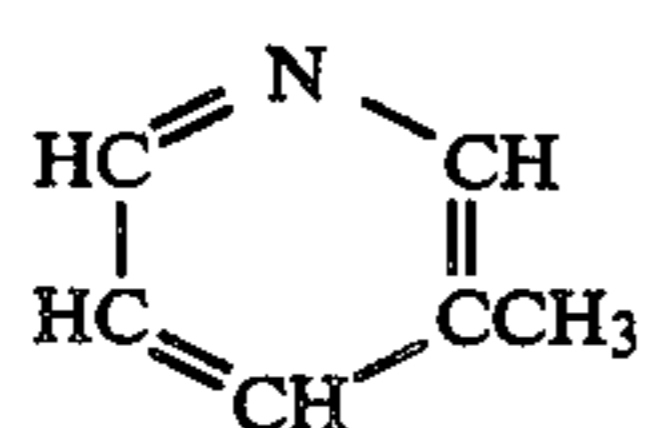
An "extract component" is a type of compound or a compound, such as a particular isomer, that is more selectively adsorbed by the adsorbent while a "raffinate component" is a compound or type of compound that is less selectively adsorbed. In this process, the gamma-isomer or beta and gamma isomers are extract components and the alpha-isomer or alpha and beta isomers are raffinate components. The term "raffinate stream" or "raffinate output stream" means a stream through which a raffinate component is removed from an adsorbent. The composition of the raffinate stream can vary from essentially 100% desorbent material (hereinafter defined) to essentially 100% raffinate components. The term "extract stream" or "extract output stream" shall mean a stream through which an extract material which has been desorbed by a desorbent material is removed from the adsorbent. The composition of the extract stream, likewise, can vary from essentially 100% desorbent material to essentially 100% extract components. Although it is possible by the process of this invention to produce high-purity extract product (hereinafter defined) or a raffinate product (hereinafter defined) at high recoveries, it will be appreciated that an extract component is never completely adsorbed by the adsorbent, nor is a raffinate component completely non-adsorbed by the adsorbent. Therefore, small amounts of a raffinate component can appear in the extract stream, and likewise, small amounts of an extract component can appear in the raffinate stream. The extract and raffinate streams then are further distinguished from each other and from the feed mixture by the ratio of the concentrations of an extract component and a specific raffinate component, both appearing in the particular stream. For example, in one embodiment, the ratio of concentration of the more selectively adsorbed gamma-isomer to the concentration of less selectively adsorbed alpha- or beta-isomer will be highest in the extract stream, next highest in the feed mixture, and lowest in the raffinate stream. Likewise, the ratio of the less selec-

tively adsorbed alpha- or beta-isomers to the more selectively adsorbed gamma-isomer will be highest in the raffinate stream, next highest in the feed mixture, and the lowest in the extract stream. The term "desorbent material" shall mean generally a material capable of desorbing an extract component. The term "desorbent stream" or "desorbent input stream" indicates the stream through which desorbent material passes to the adsorbent. When the extract stream and the raffinate stream contain desorbent materials, at least a portion of the extract stream and preferably at least a portion of the raffinate stream from the adsorbent will be passed to separation means, typically fractionators, where at least a portion of desorbent material will be separated at separation conditions to produce an extract product and a raffinate product. The terms "extract product" and "raffinate product" mean products produced by the process containing, respectively, an extract component and a raffinate component in higher concentrations than those found in the respective extract stream and the raffinate stream. The term "selective pore volume" of the adsorbent is defined as the volume of the adsorbent which selectively adsorbs extract components from a feed mixture. The term "non-selective void volume" of an adsorbent is the volume of an adsorbent which does not selectively retain an extract component from a feed mixture. This volume includes the cavities of the adsorbent which contain no adsorptive sites and the interstitial void spaces between adsorbent particles. The selective pore volume and the non-selective void volume are generally expressed in volumetric quantities and are of importance in determining the proper flow rates of fluid required to be passed into the process for efficient operations to take place for a given quantity of adsorbent.

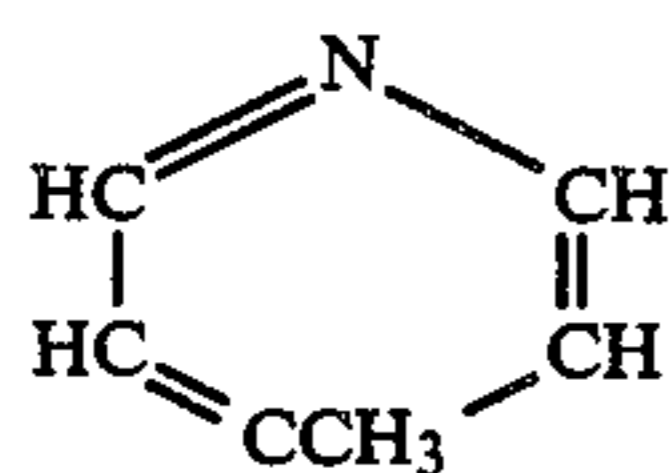
Feed mixtures which can be utilized in the process of this invention will comprise at least two picoline isomers. These isomers can be characterized by reference to Formula 1 below:



Alpha- or 2,2-methylpyridine



Beta- or 3,3-methylpyridine



Gamma or 4,4-methylpyridine

Formula 1

The major outlet for alpha-picoline is in the manufacture of 2-Vinylpyridine, which is used as part of a terpolymer consisting of styrene, butadiene, and 2-vinylpyridine. Latexes of such terpolymers are used in adhesives for bonding textiles to elastomers; the largest application is in the bonding of tire cord to rubber in the manufacture of tires. The major outlet for beta-picoline is in the manufacture of the nutritionally equivalent antipellagra vitamins, niacin and niacinamide. Gamma-picoline has been most commonly used to prepare isoniazid, an antitubercular agent. Gamma-picoline is also used in special formulations, such as for antidepressants, anticoagulants, analgesics, and other pharmaceuticals.

To separate a first picoline isomer from a feed mixture containing that isomer and at least one other picoline isomer, the mixture is contacted with the adsorbent and the first isomer is either more selectively adsorbed and retained by the adsorbent, while the other isomer is relatively unadsorbed, with the first isomer being recovered as part of the extract stream or, when the first isomer is relatively unadsorbed, it would be recovered as part of the raffinate stream. The latter type separation is referred to as a "rejective separation." The embodiment of the present invention in which a purified alpha isomer is recovered as part of the raffinate product stream is a rejective separation. The adsorbed isomer is recovered from the adsorbent by contacting the adsorbent with a desorbent material. The term "desorbent material" as used herein shall mean any fluid substance capable of removing a selectively adsorbed feed component from the adsorbent. Generally, in a swing-bed system in which the selectively adsorbed feed component is removed from the adsorbent by a purge stream, desorbent material selection is not too critical and desorbent materials comprising gaseous hydrocarbons such as methane, ethane, etc., or other types of gases such as nitrogen or hydrogen may be used at elevated temperatures or reduced pressures or both to effectively purge the adsorbed feed component from the adsorbent. However, in adsorptive separation processes which employ zeolitic adsorbents and which are generally operated continuously at substantially constant pressures and temperatures to ensure liquid phase, the desorbent material relied upon must be judiciously selected to satisfy several criteria. First, the desorbent material must displace the extract components from the adsorbent with reasonable mass flow rates without itself being so strongly adsorbed as to unduly prevent the extract component from displacing the desorbent material in a following adsorption cycle. Expressed in terms of the selectivity (hereinafter discussed in more detail), it is preferred that the adsorbent be more selective for the extract component with respect to a raffinate component than it is for the desorbent material with respect to a raffinate component. Secondly, desorbent materials must be compatible with the particular adsorbent and the particular feed mixture. More specifically, they must not reduce or destroy the critical selectivity of the adsorbent for the extract components with respect to the raffinate component. Desorbent materials to be used in the process of this invention should additionally be substances which are easily separable from the feed mixture that is passed into the process. After desorbing the extract components of the feed, both desorbent material and the extract components are typically removed in admixture from the adsorbent. Likewise, one or more raffinate components is typically withdrawn from the adsorbent in admixture with desorbent material and without a method of separating at least a portion of desorbent material, such as distillation, neither the purity of the extract product nor the purity of the raffinate product would be very high. It is therefore contemplated that any desorbent material used in this process will have a substantially different average boiling point than that of the feed mixture to allow separation of desorbent material from feed components in the extract and raffinate streams by simple fractionation thereby permitting reuse of desorbent material in the process. The term "substantially different" as used herein shall mean that the difference between the average boiling points between the desorbent material and

the feed mixture shall be at least about 5° C. The boiling range of the desorbent material may be higher or lower than that of the feed mixture.

In the preferred isothermal, isobaric, liquid-phase operation of the process of this invention, pyridine has been found to be an effective desorbent. The pyridine may be dissolved in a suitable diluent such as toluene so as to modify the rate of desorption as desired.

The prior art has recognized that certain characteristics of adsorbents are highly desirable, if not absolutely necessary, to the successful operation of a selective adsorption process. Among such characteristics are: adsorptive capacity for some volume of an extract component per volume of adsorbent; the selective adsorption of an extract component with respect to a raffinate component and the desorbent material; and, sufficiently fast rates of adsorption and desorption of the extract components to and from the adsorbent.

Capacity of the adsorbent for adsorbing a specific volume of one or more extract components is, of course, a necessity; without such capacity the adsorbent is useless for adsorptive separation. Furthermore, the higher the adsorbent's capacity for an extract component the better is the adsorbent. Increased capacity of a particular adsorbent makes it possible to reduce the amount of adsorbent needed to separate the extract component contained in a particular charge rate of feed mixture. A reduction in the amount of adsorbent required for a specific adsorptive separation reduces the cost of the separation process. It is important that the good initial capacity of the adsorbent be maintained during actual use in the separation process over some economically desirable life.

The second necessary adsorbent characteristic is the ability of the adsorbent to separate components of the feed; or, in other words, that the adsorbent possess adsorptive selectivity, (B), for one component as compared to another component. Relative selectivity can be expressed not only for one feed component as compared to another but can also be expressed between any feed mixture component and the desorbent material. The selectivity, (B), as used throughout this specification is defined as the ratio of the two components of the adsorbed phase over the ratio of the same two components in the unadsorbed phase at equilibrium conditions.

Relative selectivity is shown as Equation 1 below:

$$\text{Selectivity} = (B) = \frac{[\text{vol. percent C/vol. percent D}]_A}{[\text{vol. percent C/vol. percent D}]_U} \quad \text{Equation 1}$$

where C and D are two components of the feed represented in volume percent and the subscripts A and U represent the adsorbed and unadsorbed phases respectively. The equilibrium conditions are determined when the feed passing over a bed of adsorbent does not change composition after contacting the bed of adsorbent. In other words, there is no net transfer of material occurring between the unadsorbed and adsorbed phases.

Where selectivity of two components approaches 1.0 there is no preferential adsorption of one component by the adsorbent with respect to the other; they are both adsorbed (or non-adsorbed) to about the same degree with respect to each other. As the (B) becomes less than or greater than 1.0 there is a preferential adsorption by the adsorbent for one component with respect to the other. When comparing the selectivity by the adsorbent of one component C over component D, a (B) larger

than 1.0 indicates preferential adsorption of component C within the adsorbent. A (B) less than 1.0 would indicate that component D is preferentially adsorbed leaving an unadsorbed phase richer in component C and an adsorbed phase richer in component D. While separation of an extract component from a raffinate component is theoretically possible when the selectivity of the adsorbent for the extract component with respect to the raffinate component just exceeds a value of 1.0, it is preferred that such selectivity have a value approaching or exceeding 2. Like relative volatility, the higher the selectivity the easier the separation is to perform. Higher selectivities permit a smaller amount of adsorbent to be used in the process. Ideally, desorbent materials should have a selectivity equal to about 1 or less than 1 with respect to all extract components so that all of the extract components can be extracted as a class and all raffinate components clearly rejected into the raffinate stream.

The third important characteristic is the rate of exchange of the extract component of the feed mixture material or, in other words, the relative rate of desorption of the extract component. This characteristic relates directly to the amount of desorbent material that must be employed in the process to recover the extract component from the adsorbent; faster rates of exchange reduce the amount of desorbent material needed to remove the extract component and therefore permit a reduction in the operating cost of the process. With faster rates of exchange, less desorbent material has to be pumped through the process and separated from the extract stream for reuse in the process.

In order to test various adsorbents and desorbent material with a particular feed mixture to measure the adsorbent characteristics of adsorptive capacity and selectivity and exchange rate, a dynamic testing apparatus is employed. The apparatus consists of an adsorbent chamber of approximately 70 cc volume having inlet and outlet portions at opposite ends of the chamber. The chamber is contained within a temperature control means and, in addition, pressure control equipment is used to operate the chamber at a constant predetermined pressure. Chromatographic analysis equipment can be attached to the outlet line of the chamber and used to analyze "on-stream" the effluent stream leaving the adsorbent chamber.

A pulse test, performed using this apparatus and the following general procedure, is used to determine selectivities and other data for various adsorbent systems. The adsorbent is filled to equilibrium with a particular desorbent by passing the desorbent material through the adsorbent chamber. At a convenient time, a pulse of feed containing known concentrations of a non-adsorbed tracer (mesitylene for instance) and of the particular picoline isomers all diluted in desorbent is injected for a duration of several minutes. Desorbent flow is resumed, and the tracer and the aromatic isomers are eluted as in a liquid-solid chromatographic operation. The effluent can be analyzed by on-stream chromatographic equipment and traces of the envelopes of corresponding component peaks developed. Alternately, effluent samples can be collected periodically and later analyzed separately by gas chromatography.

From information derived from the chromatographic traces, adsorbent performance can be rated in terms of capacity index for an extract component, selectivity for one isomer with respect to the other, and the rate of

desorption of an extract component by the desorbent. The capacity index may be characterized by the distance between the center of the peak envelope of the selectively adsorbed isomer and the peak envelope of the tracer component or some other known reference point. It is expressed in terms of the volume in cubic centimeters of desorbent pumped during this time interval. Selectivity, (B), for an extract component with respect to a raffinate component may be characterized by the ratio of the distance between the center of an extract component peak envelope and the tracer peak envelope (or other reference point) to the corresponding distance between the center of a raffinate component peak envelope and the tracer peak envelope. The rate of exchange of an extract component with the desorbent can generally be characterized by the width of the peak envelopes at half intensity. The narrower the peak width the faster the desorption rate. The desorption rate can also be characterized by the distance between the center of the tracer peak envelope and the disappearance of an extract component which has just been desorbed. This distance is again the volume of desorbent pumped during this time interval.

The adsorbent to be used in the process of this invention comprises a specific crystalline aluminosilicate. Crystalline aluminosilicates such as that encompassed by the present invention include crystalline aluminosilicate cage structures in which the alumina and silica tetrahedra are intimately connected in an open three-dimensional network. The tetrahedra are cross-linked by the sharing of oxygen atoms with spaces between the tetrahedra occupied by water molecules prior to partial or total dehydration of this zeolite. The dehydration of the zeolite results in crystals interlaced with cells having molecular dimensions. Thus, the crystalline aluminosilicates are often referred to as "molecular sieves" when the separation which they effect is dependent essentially upon differences between the sizes of the feed molecules as, for instance, when smaller normal paraffin molecules are separated from larger isoparaffin molecules by using a particular molecular sieve. In the process of this invention, however, the term "molecular sieves", although widely used, is not strictly suitable since the separation of specific aromatic isomers is apparently dependent on differences in electrochemical attraction of the different isomers and the adsorbent rather than on pure physical size differences in the isomer molecules.

In hydrated form, the crystalline aluminosilicates generally encompass those zeolites represented by the Formula below:

Formula 2

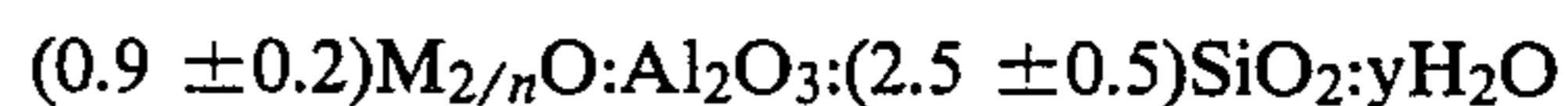


where "M" is a cation which balances the electrovalence of the tetrahedra and is generally referred to as an exchangeable cationic site, "n" represents the valence of the cation, "w" represents the moles of SiO₂, and "y" represents the moles of water. The generalized cation "M" may be monovalent, divalent or trivalent cations or mixtures thereof.

The prior art has generally recognized that adsorbents comprising the type X and the type Y zeolites can be used in certain adsorptive separation processes. These zeolites are well known to the art.

The type X structured zeolite in the hydrated or partially hydrated form can be represented in terms of mole oxides as shown in Formula 3 below:

Formula 3



where "M" represents at least one cation having a valence of not more than 3, "n" represents the valence of "M", and "y" is a value up to about 9 depending upon the identity of "M" and the degree of hydration of the crystal. As noted from Formula 3 the SiO₂/Al₂O₃ mole ratio is 2.5 ± 0.5. The cation "M" may be one or more of a number of cations such as the hydrogen cation, the alkali metal cation, or the alkaline earth cations, or other selected cations, and is generally referred to as an exchangeable cationic site. As the type X zeolite is initially prepared, the cation "M" is usually predominately sodium and the zeolite is therefore referred to as a sodium-type X zeolite. Depending upon the purity of the reactants used to make the zeolite, other cations mentioned above may be present, however, as impurities.

The type Y structured zeolite in the hydrated or partially hydrated form can be similarly represented in terms of mole oxides as in Formula 4 below:

Formula 4



where "M" is at least one cation having a valence not more than 3, "n" represents the valence of "M", "w" is a value greater than about 3 up to 6, and "y" is a value up to about 9 depending upon the identity of "M", and the degree of hydration of the crystal. The SiO₂/Al₂O₃ mole ratio for type Y structured zeolites can thus be from about 3 to about 6. Like the type X structured zeolite, the cation "M" may be one or more of a variety of cations but, as the type Y zeolite is initially prepared, the cation "M" is also usually predominately sodium.

The present invention is based on the discovery that the type Y zeolite with alkaline earth or iron group cations at exchangeable cation sites is more selective for the beta and gamma isomers of picoline than for the alpha isomers, and that the type X zeolite having potassium cations at exchangeable cationic sites, and the type Y zeolite having calcium cations at exchangeable cationic sites is more selective for the gamma than the other isomers.

Typically, adsorbents used in separative processes contain the crystalline material dispersed in an amorphous material or inorganic matrix, having channels and cavities therein which enable liquid access to the crystalline. Silica, alumina, or mixtures thereof are typical of such inorganic matrix materials. The binder aids in forming or agglomerating the crystalline particles which otherwise would comprise a fine powder. The adsorbent may thus be in the form of particles such as extrudates, aggregates, tablets, macrospheres or granules having a desired particle range, preferably from about 16 to about 60 mesh (Standard U.S. Mesh). Less water content in the adsorbent is advantageous from the standpoint of less water contamination of the product.

The adsorbent may be employed in the form of a dense fixed bed which is alternatively contacted with a feed mixture and a desorbent material in which case the

process will be only semicontinuous. In another embodiment, a set of two or more static beds of adsorbent may be employed with appropriate valving so that a feed mixture can be passed through one or more adsorbent beds of a set while a desorbent material can be passed through one or more of the other beds in a set. The flow of a feed mixture and a desorbent material may be either up or down through an adsorbent in such beds. Any of the conventional apparatus employed in static bed fluid-solid contacting may be used.

Moving bed or simulated moving bed flow systems, however, have a much greater separation efficiency than fixed bed systems and are therefore preferred. In the moving bed or simulated moving bed processes, the retention and displacement operations are continuously taking place which allows both continuous production of an extract and a raffinate stream and the continual use of feed and displacement fluid streams. One preferred embodiment of this process utilizes what is known in the art as the simulated moving bed countercurrent flow system. In such a system, it is the progressive movement of multiple liquid access points down a molecular sieve chamber that simulates the upward movement of molecular sieve contained in the chamber. Reference can also be made to D. B. Broughton's U.S. Pat. No. 2,985,589, in which the operating principles and sequence of such a flow system are described, and to a paper entitled, "Continuous Adsorptive Processing—A New Separation Technique" by D. B. Broughton presented at the 34th Annual Meeting of the Society of Chemical Engineers at Tokyo, Japan on Apr. 2, 1969, both references incorporated herein by reference, for further explanation of the simulated moving bed countercurrent process flow scheme.

Another embodiment of a simulated moving bed flow system suitable for use in the process of the present invention is the cocurrent high efficiency simulated moving bed process disclosed in U.S. Pat. No. 4,402,832 to Gerhold, incorporated by reference herein in its entirety.

It is contemplated that at least a portion of the extract output stream will pass into a separation means wherein at least a portion of the desorbent material can be separated at separating conditions to produce an extract product containing a reduced concentration of desorbent material. Preferably, but not necessary to the operation of the process, at least a portion of the raffinate output stream will also be passed to a separation means wherein at least a portion of the desorbent material can be separated at separating conditions to produce a desorbent stream which can be reused in the process and a raffinate product containing a reduced concentration of desorbent material. Typically the concentration of desorbent material in the extract product and the raffinate product will be less than about 5 vol. % and more preferably less than about 1 vol. %. The separation means will typically be a fractionation column, the design and operation of which is well known to the separation art.

Although both liquid and vapor phase operations can be used in many adsorptive separation processes, liquid-phase operation is preferred for this process because of the lower temperature requirements and because of the higher yields of an extract product that can be obtained with liquid-phase operation over those obtained with vapor-phase operation. Adsorption conditions will include a temperature range of from about 20° C. to about 250° C. with about 100° C. to about 200° C. being more

preferred and a pressure sufficient to maintain liquid phase. Desorption conditions will include the same range of temperatures and pressure as used for adsorption conditions.

The size of the units which can utilize the process of this invention can vary anywhere from those of pilot-plant scale (see for example U.S. Pat. No. 3,706,812) to those of commercial scale and can range in flow rates from as little as a few cc an hour up to many thousands of gallons per hour.

The following examples are presented for illustration purposes and more specifically are presented to illustrate the selectivity relationships that make the process of the invention possible. Reference to specific cations, desorbent materials, feed mixtures and operating conditions is not intended to unduly restrict the scope and spirit of the claims attached hereto.

EXAMPLE I

In this experiment, a series of three pulse tests were performed to evaluate the ability of the present invention to separate picoline isomers. The adsorbent used was a Y structured zeolite and a small portion of amorphous binder material with the zeolite cation exchanged with cobalt, nickel, and calcium cations in the first, second, and third tests, respectively. The adsorbent was dried to essentially complete dryness at 500° C. before it was utilized in the process in each test.

The testing apparatus was the above described pulse test apparatus. For each pulse test, the column was maintained at a temperature of 155° C. and a pressure of 100 psig to maintain liquid-phase operations. Gas chromatographic analysis equipment was attached to the column effluent stream in order to determine the composition of the effluent material at given time intervals. The feed mixture employed for each test comprised pulses which contained about 0.5 gm each of the picoline isomers, 0.25 gm mesitylene which was used as a tracer and 1.25 gm desorbent material. The desorbent material comprised 30 vol. % pyridine, with the remainder being toluene. The operations taking place for each test were as follows. The desorbent material was run continuously at a nominal liquid hourly space velocity (LHSV) of 1.0. At some convenient time interval, a pulse of the feed mixture was introduced. The desorbent stream was then resumed at 1 LHSV and continued to pass into the adsorbent column until all of the feed components had been eluted from the column as determined by observing the chromatograph generated by the effluent material leaving the adsorption column.

The results of the three tests of this Example are shown on the accompanying FIGS. 1, 2 and 3 which comprise the chromatographic traces. Gross retention volumes and selectivities derived from the traces are given on the Figures.

It is clear from all three tests that the rejective separation of alpha-picoline from the other isomers is readily achieved by the process of the present invention. There is minimal overlap between the alpha curves and curves for the beta and gamma isomers. Selectivities for both the beta and gamma isomers relative to the alpha are very high.

EXAMPLE II

The tests of Example I were repeated, except that the adsorbent used in a first test was a type X potassium exchanged zeolite and in a second test, for comparison purposes, a sodium exchanged type X zeolite, the latter

adsorbent not within the group of adsorbents for use in the present invention.

The results of the above two tests are shown on the accompanying FIGS. 4 and 5.

It is clear from FIGS. 4 and 5 that only the adsorbent of the present invention (KX-type zeolite) exhibits acceptable selectivity for the gamma picoline. In contradistinction, the separation obtained by the NaX type zeolite is very poor, with almost a complete congruence between the curves for the gamma and beta isomers.

Further reference should be made to FIG. 3, which also illustrates the embodiment of the present invention for separation of the gamma-picoline isomer. The gamma isomer separation shown in FIG. 3 is not as good as that shown in FIG. 4, but it is probably good enough for a commercial application, particularly when it is considered that both the alpha and gamma isomers may be obtained in high purity from the same separation.

I claim as my invention:

1. A process for separating alpha-picoline from a feed mixture comprising alpha-picoline and at least one other isomer of picoline, which comprises contacting said mixture at adsorption conditions with an adsorbent comprising a type Y zeolite having alkaline earth or iron group cations at exchangeable cationic sites, selectively adsorbing said other isomer to the substantial exclusion of the alpha isomer, and recovering high purity alpha-picoline as a raffinate stream.

2. The process of claim 1 wherein said feed mixture contains alpha, beta and gamma picoline.

3. The process of claim 1 wherein said other isomer is removed from said adsorbent by contacting said adsorbent with a desorbent material at desorption conditions to remove said other isomer as an extract stream.

4. The process of claim 3 wherein said desorbent material comprises pyridine.

5. The process of claim 4 wherein said cations at exchangeable cationic sites comprise cations of cobalt, nickel or calcium.

6. The process of claim 3 wherein said adsorption and desorption conditions comprise a temperature from about 20° C. to about 250° C.

7. The process of claim 1 wherein said process is effected with a simulated moving bed flow system.

8. The process of claim 7 wherein said simulated moving bed flow system is of the countercurrent type.

9. The process of claim 7 wherein said simulated moving bed flow system is of the co-current high efficiency type.

10. The process of claim 1 wherein said zeolite is dispersed in an amorphous inorganic oxide matrix.

11. A process for separating gamma-picoline from a feed mixture comprising gamma-picoline and at least one other isomer of picoline, which comprises contacting said mixture at adsorption conditions with an adsorbent comprising a type X zeolite having potassium cations at exchangeable cationic sites, or a type Y zeolite having calcium cations at exchangeable cationic sites, selectively adsorbing said gamma isomer to the substantial exclusion of the remaining isomers, removing said remaining isomers from contact with said adsorbent, and thereafter recovering high purity gamma-picoline.

12. The process of claim 11 wherein said feed mixture contains alpha, beta and gamma picoline.

13. The process of claim 11 wherein said gamma-picoline is recovered by contacting said adsorbent with a desorbent material at desorption conditions to remove said gamma isomer as an extract stream.

14. The process of claim 13 wherein said desorbent material comprises pyridine.

15. The process of claim 11 wherein said adsorption and desorption conditions comprise a temperature from about 20° C. to about 250° C.

16. The process of claim 11 wherein said process is effected with a simulated moving bed flow system.

17. The process of claim 16 wherein said simulated moving bed flow system is of the countercurrent type.

18. The process of claim 16 wherein said simulated moving bed flow system is of the co-current high efficiency type.

19. The process of claim 11 wherein said zeolite is dispersed in an amorphous inorganic oxide matrix.

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